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Study of metal injection molding of highly porous titanium by physical modeling and direct experiments

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ABSTRACT

The prospects of metal injection molding (MIM) technique for manufacturing of highly porous titanium parts was studied by physical modeling, based on feedstock warm compaction experiments. The space holder method and typical MIM binder were used in all cases of the study. The influence of the starting powder (dehydrided and atomized) in feedstock on resulting properties of porous titanium was investigated. The size of space holder particles and space holder amount were adjusted to obtain porosity and pore size desired for medical implants application. NaCl and KCl were studied and compared as prospective space holder materials. The porous samples were characterized regarding their microstructure, uptake of interstitial contents and mechanical properties. For comparison, same investigations have been conducted on samples, which were prepared by established space holder technology based on cold isostatic pressing (CIP) and sintering. Finally, first direct MIM experiments and attempts of feedstock optimization were carried out. The peculiarities and problems of metal injection molding of highly porous titanium have been discussed.

1. Introduction

Highly porous titanium (Ti) attracts attention of both materials engineers and physicians because of its growing application in production of medical implants. An easy control of porosity and geometry of pores allows manufacturing of porous titanium with elastic modulus typical for natural bones and size of pores suitable for ingrowth of soft tissues and natural fixation of implants. To achieve related structures of porous titanium, powder metallurgy route including application of a temporary space holder material is a promising approach. The conventional space holder method is employed by die or cold isostatic pressing (CIP) of mixture of titanium and space holder powders, space holder removal and sintering. At present, the most commonly used space holders are ammonium hydrogen carbonate (NH_4HCO_3) and carbamide ($CO(NH_2)_2$) which may be easily removed by thermal decomposition at temperatures below 150 °C before sintering.

The most of the medical implants possess a complex geometrical shape, which can not be directly achieved by die or cold isostatic pressing. Laptev et al. (2004) showed the possibility of shaping of cold pressed titanium parts by machining of green, space holder containing compacts. At the same time, machining in green state and space holder removal prior to sintering requires relatively high strength of green powder compacts, which may be achieved only by the use of irregular titanium powders as starting material. However, it is difficult to find on the market this type of powders with impurities level better than grade 4 (standard ASTM 67-06), which creates the risk of embrittlement in the case of further interstitials uptake during processing. Even when using irregular titanium powder, the machining of green compacts has limitations in the case of complex geometries (e.g. threads) and thin cross sections due to low stability of pressed compacts. Besides, Bram et al. (2003) also have shown that machining of sintered porous titanium parts leads to the closure of surface pores, enhanced wear of the cutting tool and to the contamination of porous structure by the wear products. Thus the manufactures of titanium highly porous titanium implants faced two problems: difficulties in shaping of implants while maintaining the open porosity on the surface and increase of oxygen content over the acceptable level. A detailed discussion on the risk of interstitial uptake during powder metallurgical

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processing of titanium and its influence on the mechanical properties is given by Baril (2010).

Both of these problems can be potentially solved by using of metal injection molding (MIM) technique. A patent published by Nelles et al. (2002) generally describes the principle of this approach and claims sodium chloride (NaCl) and potassium chloride (KCl) as suitable space holder materials. Nishiyabu et al. (2005a,b) firstly demonstrated the potential of this method for manufacturing of net-shaped parts with functional macro pores. He introduced poly (methyl methacrylate) (PMMA) as an alternative space holder material even suitable for the MIM application. A comprehensive summary of Nishiyabu's work was recently published elsewhere (Nishiyabu, 2012). Later on, several approaches of MIM application for production of porous implants from titanium powders were reported. Baril et al. (2008) developed a powder metallurgical method to deposit porous titanium coatings on dental implants produced by MIM. Chen et al. (2009) produced porous titanium cylinders by MIM using titanium powder, manufactured by hydrogenation-dehydrogenation (HDH) method, and NaCl as a space holder. The samples with NaCl content up to 60% were successfully produced. At a NaCl content of 70 vol.%, deformation and collapse of samples during debinding was observed. Engin et al. (2011) used gas atomized Ti6AlV4 powder and PMMA as space holder. After space holder removal by PMMA decomposition at 600 °C and following sintering, significant increase in oxygen and carbon contents which far exceeded the acceptable level defined by ASTM were noticed. Cysne Barbosa et al. (2013) demonstrated the manufacturing of net-shaped titanium spine implants with gradient in porosity by Two Component Injection Molding (2C-MIM). In these experiments, argon atomized titanium powder which can be supplied with qualities down to grade 1 was used. This study has shown that, working with MIM feedstock containing more than 50 vol.% space holder in a solid load (titanium and space holder powders) is a challenging task. Imwinkelried (2007) has shown that space holder content and resulting porosity of titanium implants above 65 vol.% is required to achieve percolation of the space holder. This percolation is the prerequisite to achieve a network of interconnected macro pores after sintering enabling bone ingrowth. Lower space holder percentage results in limitation of interconnected porosity and causes partly closed surface porosity, both undesired in implant applications. Therefore, further efforts are necessary to make metal injection molding suitable for production of porous titanium implants with open and interconnected macro porosity over 65%.

It should be pointed out that direct use of a standard MIM machine for processing of feedstock with increased space holder content has certain restrictions caused by machine design. During metal injection molding the feedstock is rammed forward through the MIM machine nozzle into the mold sprue through the small opening (gate) and then in the mold cavity. This results in separation of binder and particles and clogging of the nozzle if the particle size and solid load concentration are too large. The problem can be apparently solved by redesign and modification of the injection system of the standard MIM machine. However, before doing this costly work, the prospects and peculiarities of the production of highly porous titanium by MIM have to be studied by simplified physical or mathematical modeling. For this purpose, in the present paper, we focused on the procedure of the MIM physical modeling by feedstock warm compaction (WC). Another reason for small scale modeling is to avoid the need of a large amount of feedstock for each direct MIM experiment and time consuming cleaning of the injection system and the mold. The large scale preparation of feedstock under the laboratory conditions is not practical, especially if many different compositions have to be systematic investigated for feedstock optimization. Moreover, the feedstock warm compaction may be discussed as an individual way of obtaining highly porous materials. Similar technology was used, for instance, by Nishiyabu et al. (2005a,b) for production of porous graded stainless steel discs. But in the present paper feedstock warm compaction was rather used as a physical model of MIM.

Selection of the most suitable space holder powder is another key issue in production of highly porous titanium by metal injection molding. The space holder should (i) not react with the binder system, which is for instance a mixture of paraffin wax, polyethylene and stearic acid, (ii) have sufficient mechanical strength to endure conditions faced during feedstock preparation and following injection molding, (iii) remain stable at MIM temperature which is typically up to 200 °C, (iv) be insoluble in debinding media, e.g. hexane, (v) promote the pressure transfer between Ti powder particles and densification of their network, as injection pressures in conventional MIM equipment is relatively small (about 100 MPa), (vi) be fully removable in a reasonable dwell time and at low temperatures to reduce the risk of titanium contamination above established by grade 4, (vii) be available with particles size of a few hundred microns enabling the formation of interconnected pores with the size optimum for bone ingrowth and formation of blood vessels.

Commonly used space holders such as ammonium hydrogen carbonate and carbamide do not meet the requirement (iii) because they decompose at temperatures below 150 °C. Therefore, in the present paper powders of sodium chloride (NaCl) and potassium chloride (KCl) salts were used as alternative space holders. Both of them have melting points much above 200 °C and do not react with titanium at this temperature. These salts may be removed before sintering by desalination in hot water. The salts are available as powders with particles of different size including particles within several hundred microns range.

In the present study, together with the space holders mentioned above, atomized and dehydrided titanium powders and typical MIM binder system were used in feedstock preparation and the resulting structures were compared. To explore the potential of MIM, the highly porous samples were obtained by warm compaction of the feedstock, characterized and compared with porous samples manufactured by conventional space holder technique, which includes CIP, space holder removal and sintering. Thereafter, several experiments on a standard MIM machine were carried out aiming at increasing the space holder content and optimizing the feedstock composition.

2. Experimental

2.1. Starting powders

Argon atomized titanium powder (TLS Technik GmbH, Bitterfeld, Germany) and dehydrided titanium powder (Alfa Aesar, Ward Hill, MA, USA) were used in experiments. In house determined impurity contents of started powders, characteristics of particles size distribution and tap densities are summarized in Table 1. Morphologies of the titanium powders used are shown in Fig. 1a and b. The spherical gas atomized powder was slightly coarser then the irregular dehydrided one. The oxygen percentage in the gas atomized titanium powder corresponds to commercially pure titanium with low oxygen content, i.e. grade 1. On the other hand, the oxygen content of dehydrided titanium powder far exceeds the maximal standard value for titanium with high oxygen percentage, i.e. grade 4.

Sodium chloride (NaCl) (Applichem, Darmstadt, Germany) and potassium chloride (KCl) (Sigma–Aldrich, Steinheim, Germany) powders were used as space holders. The morphologies of NaCl and KCl particles are presented in Fig. 1c and d, respectively. NaCl particles were nearly cubic in shape, whereas KCl particles had a